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From chemical data (1), ethylene imine appears to be a three membered heterocyclic ring similar to cyclopropane and ethylene oxide. It has a very high boiling point, 55°C, as compared with ——34°C for cyclopropane and 13°C for ethylene oxide. This has been taken as evidence of strong hydrogen bonding in the liquid, and is supported by the strongly basic character of the imine nitrogen atom. Ethylene imine readily polymerizes to viscous, oily, chain type polymers in the presence of carbon dioxide or mild oxidizing agents. However, Jones and co-workers (2) have reported that ethylene imine polymerizes to a negligible amount at room temperature in the absence of such catalysts.

The sample of ethylene imine studied was prepared by a modification (3) of Wenker's method (4), treating ethanolamine with sulfuric acid and splitting out sulfuric acid with sodium hydroxide to close the ring. The sample was dried over potassium hydroxide and metallic sodium and distilled through an efficient column. The sample used boiled within a one degree range about the reported boiling point. The Raman and infrared spectra were obtained within a few days after preparation of the sample. Portions of ethylene imine not in use were frozen in ampules which were thoroughly evacuated and sealed off to prevent polymerization.

A start toward interpretation of the spectrum of ethylene imine can be made by comparison with the known spectra of ethylene oxide and cyclopropane. Each of these molecules is nearly, or exactly, an equilateral triangle. The masses of the oxygen atom, the imino group, and the methylene group are nearly the same; 16, 15, and 14 atomic weight units respectively. Furthermore, since these three molecules are isoelectronic, we may expect the force constants for the three molecules to be on the same order of magnitude.

We may expect, however, that the observed spectra of these three molecules will be quite different in selection rules due to the different symmetry of the molecules. Cyclopropane is of point group D_{3h}, and is seen to have six frequencies active only in the Raman, two frequencies active only in the infrared, four frequencies active in both the Raman and infrared, and two completely inactive frequencies. Ethylene oxide, of point group C_{2v}, has twelve frequencies active both in the Raman and infrared, and three frequencies active only in the Raman. Ethylene imine, of point

group C_s, has eighteen fundamentals active both in the Raman and infrared. Of these, ten should be polarized in the Raman and eight depolarized. The eight bands which are depolarized in the Raman should show a type A band shape in the infrared, produced when the shift in electric moment is parallel to the least moment of inertia. The ten totally symmetric bands should show a hybrid structure composed of some mixture of type B and C, since the shift in electric moment lies in the plane of the major and intermediate axis of inertia, but not necessarily in the direction of either axis. The curves shown here are estimated from the curves of Badger and Zumwalt (5), assuming that the moments of inertia of ethylene imine are the same as those of ethylene oxide which have been determined very accurately by microwave spectra (6).

The Raman spectrum of ethylene imine has been determined by Kohlrausch and Reitz, including polarization data (7). Kohlrausch listed three frequencies, at 786, 910, and 1277 wave numbers, as dubious and suggested they might be due to impurities. The Raman spectrum of ethylene imine has therefore been rechecked with a Lane-Wells spectrograph, using a two inch long Raman tube and a one-half hour exposure. Not all the lines reported by Kohlrausch were observed, since he used exposures up to 100 hours, but the significant fact is that the line at 786 wave numbers appears in our short run and can scarcely be attributed to a minor impurity.

Table 1

Observed Spectrum of Ethylene Imine in the Infrared

Fundamentals			Combinations and Overtones	
Int.	(Species)	Shape V (cm^{-1})	V (cm^{-1})	
764	s	A′	1548	1528 = 2 x 764
794	w	A″	1642	1651 = 794 + 857
857	s	A′	1663	1665 = 900 + 765
900	w	A″	1767	1765 = 1000 + 765
1000	w	A′	1815	1800 = 2 x 900
1095	w	A′	1865	1857 = 1000 + 857
1132	vw	--	1975	1989 = 857 + 1132
1215	vw	--	1995	2000 = 2 x 1000
1235	s	--	2048	2032 = 900 + 1132
1269	w	--	2092	2092 = 857 + 1235
1446	ms	--	2204	2211 = 1446 + 765
1467	m	--	2254	2249 = 1484 + 765
1484	ms	--	2470	2470 = 2 x 1235
2990	vs	--	2555	2566 = 1467 + 1095
3365	s	--	3470	?
			3886	3890 = 2990 + 900

Table 2

Assignments for Ethylene Imine
(Ethylene Oxide Listed for Comparison)

	C_2H_4NH			C_2H_4O	
A′	twist	764	B_2	twist	704
A″	twist	1000	A_2	twist	1023
A′	rock	1095	B_2	rock	1153
A″	rock	900	A_2	rock	1379 ?
A′	bend	1235	B_1	bend	1153
A″	bend	1132	A_1	bend	1120
	NH bend	1269		------	
	NH bend	1484		------	
A′	CH_2 def.	1446	B_1	CH_2 def.	1469
A″	CH_2 def.	1467	A_1	CH_2 def.	1487
A″	ring	794	B_1	ring	806
A′	ring	856	A_1	ring	863
A″	ring	1215	A_1	ring	1267
A′	CH stretch	2935	A_1	CH stretch	3007
A′	CH stretch	2998	B_1	CH stretch	3007
A″	CH stretch	2990	A_2	CH stretch	3061
A″	CH stretch	3060	B_2	CH stretch	3061
A′	NH stretch	3311			

The infrared spectrum of ethylene imine has been determined from 400 to 4000 wave numbers, using a Perkin Elmer spectrometer with potassium bromide, sodium chloride, and lithium fluoride prisms. For the low frequency bands, where the band envelope has been fairly well resolved, the species as determined from the shape of the band has been included. These values do not check too well with the Raman frequencies, since the infrared spectrum is of the gas and the Raman spectra spectrum of the liquid. The strong hydrogen bonding in the liquid would be expected to shift the frequencies considerably.

From these data, a tentative assignment of fundamentals has been made. In making these assignments, the following factors have been taken into account: the Raman polarization, distinguishing totally symmetric and non-totally symmetric fundamentals; the infrared band shape where it is resolvable, also distinguishing non symmetric from symmetric fundamentals; approximate intensities, distinguishing fundamentals from combinations; and the frequency of certain fundamentals which are characteristic of certain groups of atoms in the molecule. For example, the strong frequency near 3365 wave numbers is certainly the N-H stretching vibration; the set of frequencies near 3000 wave numbers are to be assigned to

Table 3

Force Constants for Ethylene Oxide
(Megadynes / cm)

Constant	Computed from Observed Frequencies	Estimated from Badger's Rule	Ring Freq. C_2H_4O	Ring Freq. C_2H_4NH
C-C	0.492	0.510	806	794
C-O	0.430	0.440	863	856
			1267	1215

C-H stretching vibrations; the two frequencies at 1446 and 1467 wave numbers are CH_2 deformation frequencies. The three frequencies of the ring itself, considered as a three particle system, lie at 1215, 855, and 818 wave numbers. These three ring frequencies should be strong in the Raman, and in fact are the three strongest fundamentals below 2000 wave numbers. However, two of these three frequencies are depolarized, while the symmetry of the molecule requires that but one of these frequencies be depolarized. An analogous situation occurs in the spectrum of ethylene oxide, where again two of the obvious choices for ring frequencies are depolarized. Linnett (8) has attempted to explain away this discrepancy by assigning two overlapping fundamentals, which coincidence might invalidate polarization measurements of the lowest ring frequency. However, specific heat data by Kistiakowsky and Rice (9) seem to preclude the possibility of two frequencies in this range, and since this same problem arises in the ethylene imine spectrum it is hard to explain why a chance coincidence of lines should occur in two different spectra. It appears more reasonable to assume that one of the two lower ring frequencies is totally symmetric but has a rho value of 6/7 in each of these two molecules. The assignment of the remaining frequencies to specific modes of vibration is much less certain, since these rocks, wags, and twists are not assigned with certainty even for ethylene oxide, where the higher symmetry makes assignment easier.

A calculation of the three ring frequencies of ethylene oxide has been made on the basis of the theory of small vibrations, using a hybrid of valency and central forces involving two stretching and one bending force constants. Using the reported ring frequencies, 806,863, and 1267 wave numbers, the computed value for the C-C force constant is 0.492 megadynes and that for the C-O force constant is 0.430 megadynes. These calculated force constants are compared with expected values based on Badger's rule (10). The fre-

quencies assigned to the ring in ethylene imine are shown for comparison. From the closeness of the check there appears little doubt that these particular frequencies are correctly assigned.

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